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13. ABSTRACT (Maximum 200 words)  Interaction of some 8-hydroxyquinoline-substituted and related ligands (see Figure 1) with various metal ions was evaluated by a calorimetric titration technique at 25°C in MeOH. Bis-(8-hydroxyquinoline-2-ylmethyl)-substituted ligand 13 forms a very strong complex with Ba <sup>2+</sup> (log K = 11.6 in MeOH) and is highly selective for Ba <sup>2+</sup> over Na <sup>+</sup> , K <sup>+</sup> , Zn <sup>2+</sup> and Cu <sup>2+</sup> (selectivity factor > 10 <sup>6</sup> ). The <sup>1</sup> H NMR spectral studies of the Ba <sup>2+</sup> complexes with bis-(8-hydroxyquinoline-2-ylmethyl)- and bis(5,7-dichloro-8-hydroxyquinoline-2-ylmethyl)-substituted diaza-18-crown-6 ligands (13 and 10) suggest that these complexes are cryptate-like structures with two overlapping hydroxyquinoline rings forming a pseudo second macroring.				
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**Metal Ion Complexation Studies of Novel 8-Hydroxyquinoline-Containing  
Diaza-18-Crown-6 Ligands and Analogues**

by

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**Table 1.** Log  $K$ ,  $\Delta H$  (kJ/mol), and  $T\Delta S$  (kJ/mol) Values for Interactions of Macrocyclic Ligands with Metal Ions in Methanol Solution at 25.0 °C

ligand	cation	log $K$	$\Delta H$	$T\Delta S$
<b>1<sup>a</sup></b>	Na <sup>+</sup>	2.89	-14.1	2.4
	K <sup>+</sup>	3.39	-24.4	-5.0
	Mg <sup>2+</sup>	6.82	-2.5	36.4
	Ba <sup>2+</sup>	3.60	-11.6	8.9
	Zn <sup>2+</sup>	5.12	-11.4	-8.5
	Cu <sup>2+</sup>	10.1	-92.5	-34.9
	Co <sup>2+</sup>	5.14	-91.1	-61.8
<b>2<sup>a</sup></b>	Na <sup>+</sup>	3.74	-26.4	-5.1
	K <sup>+</sup>	6.61	-58.1	-20.4
	Mg <sup>2+</sup>	b		
	Ca <sup>2+</sup>	4.71	-25.2	1.7
	Sr <sup>2+</sup>	4.67	-24.6	2.1
	Ba <sup>2+</sup>	12.2	-76.1	-6.5
<b>4</b>	Mg <sup>2+</sup>	5.7 ± 0.2	10.7 ± 0.9	43.2
	Co <sup>2+</sup>	3.91 ± 0.08	-91.2 ± 0.5	-68.9
<b>5</b>	Mg <sup>2+</sup>	5.02 ± 0.08	13.9 ± 0.9	42.6
	Co <sup>2+</sup>	3.96 ± 0.06	-84.5 ± 0.5	-61.9
<b>6</b>	K <sup>+</sup>	b		
	Ba <sup>2+</sup>	3.57 ± 0.06	-29.4 ± 0.7	-9.0
	Zn <sup>2+</sup>	4.80 ± 0.08	-64.8 ± 0.6	-37.4
	Cu <sup>2+</sup>	5.01 ± 0.07	-57.6 ± 0.6	-29.0

...Continuation of Table 1

ligand	cation	log $K$	$\Delta H$	T $\Delta S$
8	Na <sup>+</sup>	$\sim 3^c$	$\sim -5^c$	
	K <sup>+</sup>	$3.52 \pm 0.03$	$-31.2 \pm 0.4$	-11.1
	Ba <sup>2+</sup>	$4.22 \pm 0.05$	$-19.2 \pm 0.8$	4.9
	Zn <sup>2+</sup>	$> 5.5$	$-19.0 \pm 0.5$	$> 12.4$
	Cu <sup>2+</sup>	$4.28 \pm 0.09$	$-55.3 \pm 0.7$	-30.9
13	Na <sup>+</sup>	$3.65 \pm 0.01$	$-25.3 \pm 0.2$	-4.5
	K <sup>+</sup>	$5.88 \pm 0.04^d$	$-55.6 \pm 0.7^d$	-22.0
	Ba <sup>2+</sup>	$11.6 \pm 0.2^d$	$-73.0 \pm 0.5^d$	-6.8
	Zn <sup>2+</sup>	$4.92 \pm 0.07^e$	$-95.7 \pm 0.6$	-67.6
	Cu <sup>2+</sup>	$4.39 \pm 0.09$	$-100 \pm 1$	-74.9
14	Na <sup>+</sup>	$3.02 \pm 0.05$	$-20.0 \pm 0.6$	-2.8
	K <sup>+</sup>	$3.82 \pm 0.02$	$-47.8 \pm 0.3$	-26.0
	Ba <sup>2+</sup>	$4.87 \pm 0.04$	$-26.4 \pm 0.4$	1.4
	Zn <sup>2+</sup>	$4.80 \pm 0.08$	$-64.8 \pm 0.6$	-37.4
	Cu <sup>2+</sup>	(Brown Precipitate)		

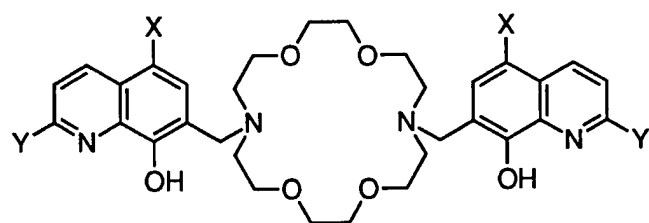
<sup>a</sup> Bordunov, A. V.; Bradshaw, J. S.; Zhang, X. X.; Dalley, N. K.; Kou, X.-L.; Izatt, R. M. *Inorg. Chem.* 1996, 35, 7229.

<sup>b</sup>No measurable heat other than heat of dilution indicating that  $\Delta H$  or/and log  $K$  is small.

<sup>c</sup>Estimated by a competitive calorimetric titration with Zn<sup>2+</sup>.

<sup>d</sup>Determined by a competitive calorimetric titration.

<sup>e</sup>When [Zn<sup>2+</sup>]/13  $\geq$  2, a white precipitate formed.

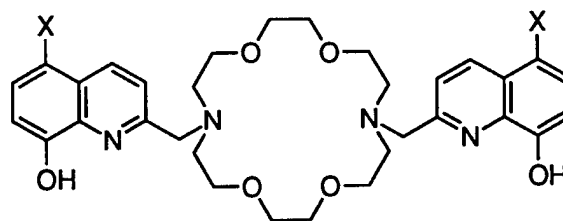


**1** X = Cl, Y = H

**4** X = Y = H

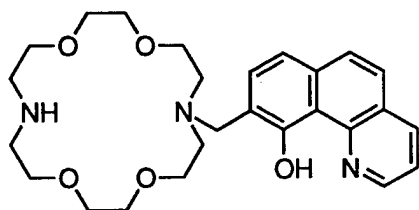
**5** X = CH<sub>3</sub>, Y = H

**6** X = H, Y = OH

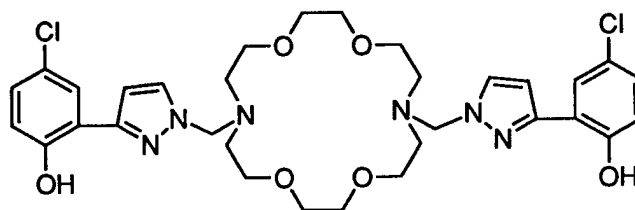


**2** X = Cl

**13** X = H



**8**



**14**

Figure 1. 5-Chloro-8-hydroxyquinoline(CHQ)-substituted Diaza-18-crown-6 Ligand Analogues of **1** and **2** Used in this Study